

PATENT ABSTRACTS OF JAPAN

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(54) ACTIVE ENERGY RAY HARDENING COMPOSITION FOR SHEET LIKE OPTICAL ARTICLES

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an active energy ray hardening composition having low viscosity, excellent in inner hardening properties of thick film, and releasing properties by including compounds having oxetane ring, or compounds having epoxy groups and a photo cation polymerization initiator.

SOLUTION: This composition includes (A) the oxetane compounds containing 1 to 4 oxetane rings, (B) the compounds containing epoxy groups (preferably, an aromatic epoxy resin, a cycloaliphatic epoxy resin), (C) compounds initiating cationic polymerization by irradiation of the active energy ray (preferably diaryliodonium salts). The component (A) is preferably compounded 10 to 95 pts.wt. per 100 pts.wt. of the sum of the component (A) and the component (B). The preferable amount of the component (C) is 0.1 to 10 wt.%. based on the sum of the component (A) and (B). This composition is expected to be suitable for manufacturing the sheet like optical articles such as a Fresnel lens, a lenticular lens or the like.

LEGAL STATUS

[Date of request for examination]

12.08.2002

[Date of sending the examiner's decision of

AN 1999:583249 CAPLUS
 DN 131:215140
 ED Entered STN: 16 Sep 1999
 TI Active energy ray-hardenable compositions for optical material sheets
 IN Nakagawa, Sumie; Igarashi, Ichiro; Sanematsu, Tetsuji
 PA Toa Gosei Chemical Industry Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 11 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C08G059-40
 ICS C08G059-68; G02B001-04; G02B003-08
 CC 37-3 (Plastics Manufacture and Processing)
 Section cross-reference(s): 38, 73

FAN.CNT 1

| | PATENT NO. | KIND | DATE | APPLICATION NO. | DATE |
|------|---------------|------|----------|-----------------|--------------|
| PI | JP 11246647 | A | 19990914 | JP 1998-64399 | 19980227 <-- |
| | JP 3671658 | B2 | 20050713 | | |
| PRAI | JP 1998-64399 | | 19980227 | | |

CLASS

| PATENT NO. | CLASS | PATENT FAMILY CLASSIFICATION CODES |
|-------------|-------|--|
| JP 11246647 | ICM | C08G059-40 |
| | ICS | C08G059-68; G02B001-04; G02B003-08 |
| | IPCI | C08G0059-40 [ICM,6]; C08G0059-68 [ICS,6]; G02B0001-04 [ICS,6]; G02B0003-08 [ICS,6] |
| | IPCR | C08G0059-00 [I,C*]; C08G0059-40 [I,A]; C08G0059-68 [I,A]; G02B0001-04 [I,A]; G02B0001-04 [I,C*]; G02B0003-08 [I,A]; G02B0003-08 [I,C*] |

AB Title compns., showing low viscosity, no cure shrinkage, good mold-releasability, and small warp in moldings, comprise (A) compds. containing 1-4 oxethane ring(s), (B) epoxy-containing compds., and (C) compds. which initiates cationic polymerization by irradiation of active energy ray.

Thus,

3-ethyl-3-phenoxymethyloxacyclobutane 75, UVR 6110 (alicyclic epoxy compound) 25, and UVI 6990 (triarylsulfonium hexafluorophosphate/propylene carbonate mixture) 2 parts were mixed to obtain a composition with viscosity 30 mPa·s (25°), which was UV-irradiated in a mold to give a lens with uniform curing, good mold release, and no warp.

ST active energy ray curable oxethane compn; epoxy compd active energy curable compn; cationic polymn initiator oxethane compn; ethylphenoxymethyloxacyclobutane alicyclic epoxy compd UV curable; lens UV curable compn mold releasability; warping prevention lens oxethane compn

IT Lenses

(UV-curable compns. containing oxethanes, epoxy compds., and cationic polymerization initiators for optical material sheets)

IT Epoxy resins, uses

RL: DEV (Device component use); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(alicyclic; UV-curable compns. containing oxethanes, epoxy compds., and cationic polymerization initiators for optical material sheets)

IT Epoxy resins, uses

RL: DEV (Device component use); PEP (Physical, engineering or chemical process); PROC (Process); USES (Uses)

(aromatic epoxy resins; UV-curable compns. containing oxethanes, epoxy compds., and cationic polymerization initiators for optical material sheets)

IT Polymerization catalysts

(cationic; UV-curable compns. containing oxethanes, epoxy compds., and cationic polymerization initiators for optical material sheets)

IT 242488-27-3P

RL: DEV (Device component use); IMF (Industrial manufacture); PEP (Physical, engineering or chemical process); PREP (Preparation); PROC (Process); USES (Uses)

DERWENT-ACC-NO: 1999-566621

DERWENT-WEEK: 200547

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TITLE: Energy beamcurable composition - for optical goods in sheet form

PATENT-ASSIGNEE: TOA GOSEI CHEM IND LTD[TOAG]

PRIORITY-DATA: 1998JP-0064399 (February 27, 1998)

PATENT-FAMILY:

| PUB-NO | PUB-DATE | LANGUAGE | PAGES | MAINIPC |
|----------------------|--------------------|----------|-------|-------------|
| JP 3671658 B2 | July 13, 2005 | N/A | 019 | C08G 059/40 |
| <u>JP 11246647 A</u> | September 14, 1999 | N/A | 011 | C08G 059/40 |

APPLICATION-DATA:

| PUB-NO | APPL-DESCRIPTOR | APPL-NO | APPL-DATE |
|--------------|-----------------|---------------|-------------------|
| JP 3671658B2 | N/A | 1998JP0064399 | February 27, 1998 |
| JP 3671658B2 | Previous Publ. | JP 11246647 | N/A |
| JP 11246647A | N/A | 1998JP0064399 | February 27, 1998 |

INT-CL (IPC): C08G059/40, C08G059/68 , G02B001/04 , G02B003/08

ABSTRACTED-PUB-NO: JP 11246647A

BASIC-ABSTRACT:

Energy beam-curable composition for optical goods in sheet form comprises components (A) a compound containing 14 oxetan rings, (B) a compound containing an epoxy group and (C) a compound which causes initiation of cationic polymerisation by irradiation of active energy beam.

USE - Used in Fresnel lens, reticular lens and a prism sheet.

ADVANTAGE - Product gives low viscosity and low shrinkage at curing, excels in mould releasability, and less warping of the cured product.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: ENERGY BEAM CURE COMPOSITION OPTICAL GOODS SHEET FORM

DERWENT-CLASS: A21 A23 A89 E13 G02 P81

CPI-CODES: A05-A02; A05-E06B; A10-E10; A11-C02B; A12-L02A; E06-A02D; E07-A03C; G02-A05;

CHEMICAL-CODES:

Chemical Indexing M3 *01*

Fragmentation Code

B614 B712 B713 B720 B744 B796 B798 B799 B832 B833
C216 C316 F012 F013 F017 F019 F100 F111 F199 F211
F299 G010 G011 G012 G013 G019 G020 G021 G029 G040
G100 G111 G112 G113 G221 G299 H02 H141 H541 H581
H582 H583 H584 H589 H601 H608 H609 H621 H622 H623
H641 H681 H682 H683 H684 H685 H689 H713 H716 H721
H722 H723 J011 J271 K442 L463 L472 L660 M113 M115
M116 M119 M121 M129 M132 M142 M143 M144 M148 M149
M150 M210 M211 M212 M213 M214 M215 M216 M220 M221
M222 M223 M224 M225 M226 M231 M232 M233 M240 M250
M262 M272 M273 M280 M281 M282 M283 M311 M312 M313
M314 M315 M316 M321 M322 M323 M331 M332 M333 M334

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the activity energy-line hardening setup-of-tooling product suitable for manufacture of sheet-like optical articles, such as a Fresnel lens, a lenticular lens, and a prism sheet.

[0002]

[Description of the Prior Art] Conventionally, as for the optical article of the shape of a sheet, such as a Fresnel lens, it was common to have been manufactured by injection molding and heat press forming of thermoplastics. However, by these manufacture approaches, long duration was needed for heating and cooling at the time of manufacture, and there was a problem that productivity was low. Then, in recent years, the approach of slushing an activity energy-line hardening setup-of-tooling product between lens mold base materials, such as metal mold or a plastic pattern, a transparency resin substrate, or a film, irradiating activity energy lines, such as ultraviolet rays, at this as the manufacture approach of the sheet-like optical article which solves the above-mentioned problem, making harden a constituent, and manufacturing has come to be adopted. The constituent hardened by the activity energy-line initiation radical polymerization which generally consists of oligomer, such as urethane (meta) acrylate, epoxy (meta) acrylate, and polyester (meta) acrylate, as an activity energy-line hardening setup-of-tooling product used for the manufacture approach concerned is used.

[0003]

[Problem(s) to be Solved by the Invention] However, generally said radical hardening type of acrylate system constituent had large hardening contraction, therefore after hardening, the sheet curved and it had the case where exfoliation and a crack with a transparence base material arose. Although there was a constituent which blended monofunctional (meta) acrylate further as a constituent which reduces this hardening contraction, since a hardened material became weak, in case a sheet was removed from a mold, it was what has the problem which breaks or is missing. Moreover, although the hardened material obtained is excellent in flexibility, since urethane (meta) acrylate had the very high viscosity of the oligomer before hardening itself, the constituent which blended urethane (meta) acrylate was that in which a bubble is bit in case a constituent is slushed into a mold, and degassing has the fault of being difficult. On the other hand, although the constituent of optical cationic polymerization nature which consists of an epoxy resin, vinyl ether, etc. had also been examined in recent years, since hardenability in case these many manufacture the hardened material of a thick film was inadequate, or a constituent did not harden enough, it was what has the fault that a cure rate is slow. Moreover, although there is also the approach of irradiating an activity energy line superfluously in order to improve hardenability, in case the hardened material obtained was hard in this case, it was weak, it became a thing without elongation and a sheet was removed from ****, it was what breaks or is missing. The constituent was hypoviscosity, this invention persons had little hardening contraction, were excellent in the mold-release characteristic from the mold after hardening, and they inquired wholeheartedly in order to find out the activity energy-line hardening setup-of-tooling product suitable for manufacturing a sheet-like optical

article with little curvature of a hardened material.

[0004]

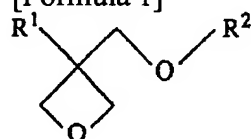
[Means for Solving the Problem] In order for this invention persons to solve said technical problem as a result of various examination, the constituent of the optical cationic polymerization mold which consists of a compound which has the compound and epoxy group which have an oxetane ring is hypoviscosity, and was excellent in the inner drying property in a thick film, and the hardened material was excellent in the mold-release characteristic from the mold, and curvature completed header this invention for few things. Hereafter, this invention is explained to a detail.

[0005]

[Embodiment of the Invention] ******(A) If it is the compound which has 1-4 oxetane rings in a molecule as a component (A) component, both a monomer and its oligomer can be used. As a compound which has one oxetane ring, the compound expressed with the following general formula (1) is mentioned into a molecule.

[0006]

[Formula 1]



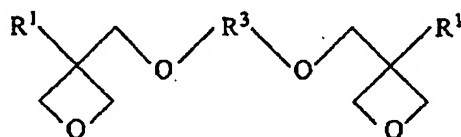
(1)

[0007] Here, it sets at a ceremony (1) and is R¹. It is a thienyl group at the alkyl group of 1-6 carbon numbers, such as a hydrogen atom, a fluorine atom, a methyl group, an ethyl group, a propyl group, and butyl, the fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group, and a furil radical list. R² The alkyl group of 1-6 carbon numbers, such as a methyl group, an ethyl group, a propyl group, and butyl, 1-propenyl radical, 2-propenyl radical, a 2-methyl-1-propenyl radical, The alkenyl radical of 2-6 carbon numbers, such as a 2-methyl-2-propenyl radical, 1-butenyl group, 2-butenyl group, and 3-butenyl group, The radical which has aromatic series rings, such as a phenyl group, benzyl, fluoro benzyl, a methoxybenzyl radical, and a phenoxy ethyl group, The radical, ethyl carbonyl group to which halogenation of the aromatic series ring was carried out in the radical which has an aromatic series ring, The alkyl carbonyl group of 2-6 carbon numbers, such as a propylcarbonyl radical, a butyl carbonyl group, and a pentyl carbonyl group, The alkoxy carbonyl group of 2-6 carbon numbers, such as an ethoxycarbonyl radical, a propoxy carbonyl group, and a butoxycarbonyl radical, The alkoxy carbamoyl group of 2-6 carbon numbers, such as an ethyl carbamoyl group, a propyl carbamoyl group, a butylcarbamoyl radical, and a pentyl carbamoyl group, etc. is mentioned to a list.

[0008] Next, the compound shown by the following general formula (2) as a compound which has two oxetane rings is mentioned.

[0009]

[Formula 2]



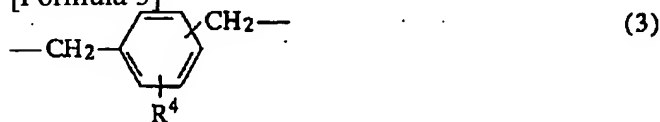
(2)

[0010] It sets at a ceremony (2) and is R¹. It is the same radical as the thing in said general formula (1). R³ For example, it is a carbonyl group etc. at the alkylene group and list containing functional groups, such as lines, such as lines, such as lines, such as ethylene, a propylene radical, and a butylene radical, or a branching-like alkylene group, a poly(ethyleneoxy) group, and the Pori (propyleneoxy) radical, or a letter Pori (alkyleneoxy) radical of branching, a pro PENIREN radical, a methyl pro PENIREN radical, and a butenylene radical, or a branching-like unsaturated hydrocarbon radical, a carbonyl group, a carboxyl group, and a carbamoyl group. Moreover, R³ It is also the polyad chosen from the radical

shown by the following type (3), (4), and (5).

[0011]

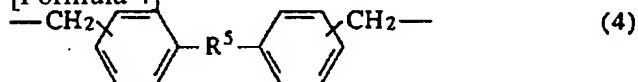
[Formula 3]



[0012] It sets at a ceremony (3) and is R4. It is a carbamoyl group at halogen atoms, such as an alkoxy group of 1-4 carbon numbers, such as 1-4 alkyl groups, such as a hydrogen atom, a methyl group, an ethyl group, a propyl group, and butyl, a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, a chlorine atom, and a bromine atom, a nitro group, a cyano group, a sulfhydryl group, a low-grade alkyl carbonyl group, a carboxyl group, and a list. Moreover, in a formula (3), halogenation of the aromatic series nucleus may be carried out.

[0013]

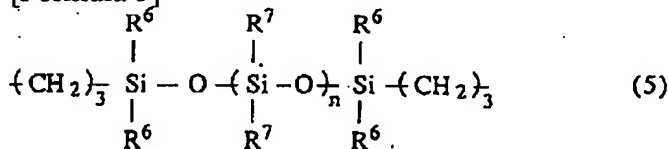
[Formula 4]



[0014] a formula (4) -- setting -- R5 An oxygen atom, a sulfur atom, a methylene group, NH, SO and SO2, and C (CF3)2 Or C(CH3) 2 it is . Moreover, in a formula (4), halogenation of the aromatic series nucleus may be carried out.

[0015]

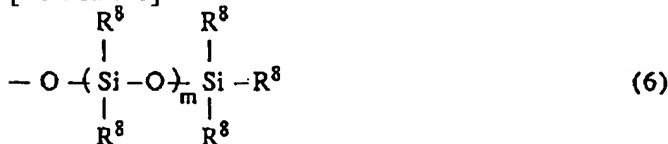
[Formula 5]



[0016] It sets at a ceremony (5) and is R6. It is an aryl group at the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, and butyl, and a list. n is the integer of 0-2000. R7 It is an aryl group at the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, and butyl, and a list. R7 It is also the radical chosen from the radical shown by the following formula (6).

[0017]

[Formula 6]

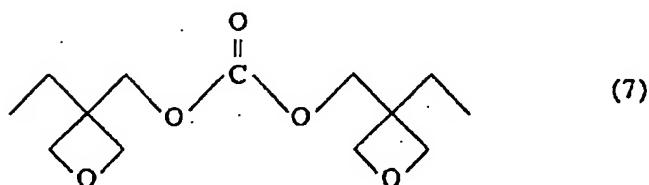


[0018] It sets at a ceremony (6) and is R8. It is an aryl group at the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, and butyl, and a list. m is the integer of 0-100.

[0019] As an example of a compound of having two oxetane rings, the compound shown by the following formula (7) and (8) is mentioned.

[0020]

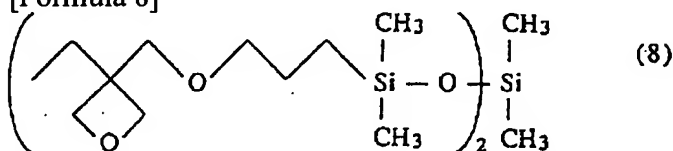
[Formula 7]



[0021] It sets at a ceremony (2) and the compound shown by the formula (7) is R1. An ethyl group and R3 It is the compound which is a carboxyl group.

[0022]

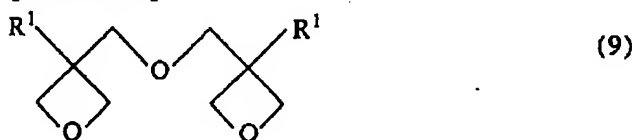
[Formula 8]



[0023] It sets at a ceremony (2) and the compound shown by the formula (8) is R1. An ethyl group and R3 It is R6 at a formula (5). And R7 They are a methyl group and the compound whose n is 1. In the compound which has two oxetane rings, there is a compound shown by the following general formula (9) as desirable examples other than the above-mentioned compound. It sets at a ceremony (9) and is R1. It is the same radical as the thing in said general formula (1).

[0024]

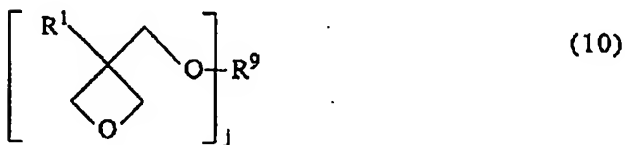
[Formula 9]



[0025] As a compound which has 3-4 oxetane rings, the compound shown by the following general formula (10) is mentioned.

[0026]

[Formula 10]



[0027] It sets at a ceremony (10) and is R1. It is the same radical as the thing in said general formula (1). R9 For example, branching-like polysiloxane radicals, such as a radical shown by a branching-like Pori (alkyleneoxy) radical and the following formulas (15), such as a branching-like alkylene group of the carbon numbers 1-12, such as a radical shown by following type (11) - (13), and a radical shown by the following formula (14), etc. are mentioned. j is 3 or 4.

[0028]

[Formula 11]



[0029] In a formula (11), R10 is low-grade alkyl groups, such as a methyl group, an ethyl group, and a propyl group.

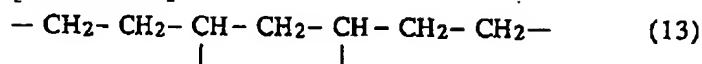
[0030]

[Formula 12]



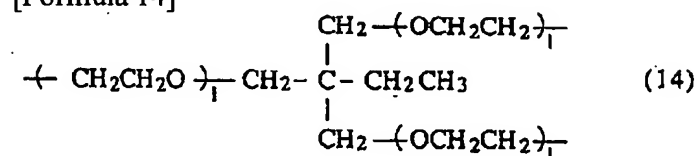
[0031]

[Formula 13]



[0032]

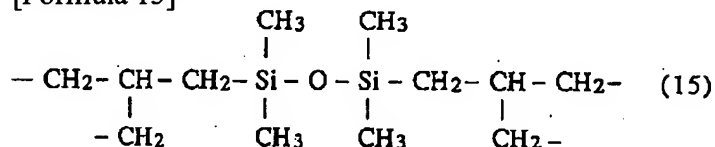
[Formula 14]



[0033] In a formula (14), l is the integer of 1-10.

[0034]

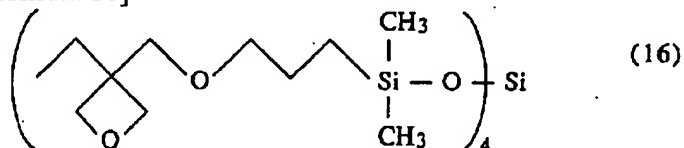
[Formula 15]



[0035] As an example of a compound of having 3-4 oxetane rings, the compound shown by the following formula (16) is mentioned.

[0036]

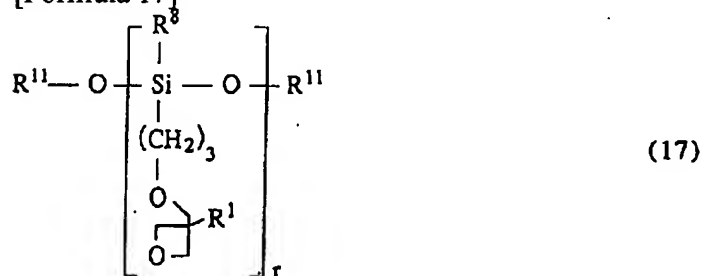
[Formula 16]



[0037] Furthermore, as an example of the compound which has 1-4 oxetane rings except having described above, there is a compound shown by the following formula (17).

[0038]

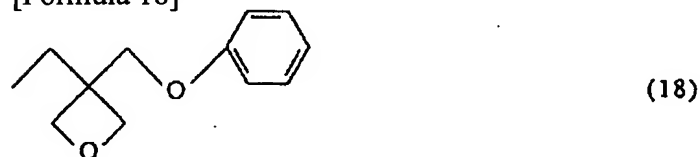
[Formula 17]

[0039] It sets at a ceremony (17) and is R⁸. It is the same radical as the thing in a formula (6). R¹¹ is a trialkylsilyl group at the alkyl group list of the carbon numbers 1-4, such as a methyl group, an ethyl

group, a propyl group, and butyl, and r is 1-4. There is a compound shown below as a desirable example of the oxetane compound used by this invention.

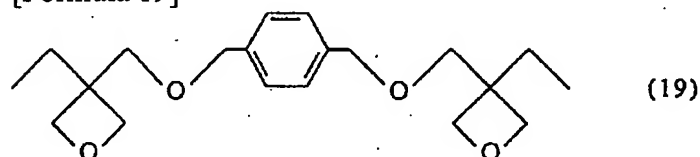
[0040]

[Formula 18]



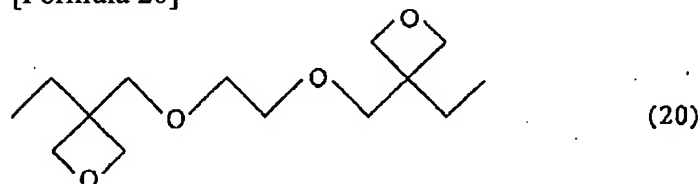
[0041]

[Formula 19]



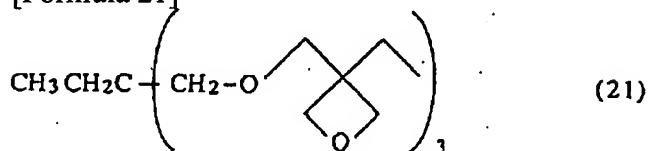
[0042]

[Formula 20]



[0043]

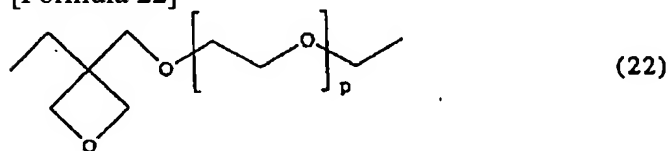
[Formula 21]



[0044] Moreover, the compound which has 1-4 oxetane rings which have the with a molecular weight of about 1000 to 5000 amount of macromolecules besides these is also mentioned. The following compounds are mentioned as these examples.

[0045]

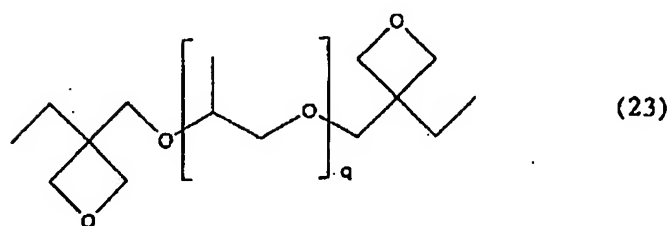
[Formula 22]



[0046] p is 20-200 here.

[0047]

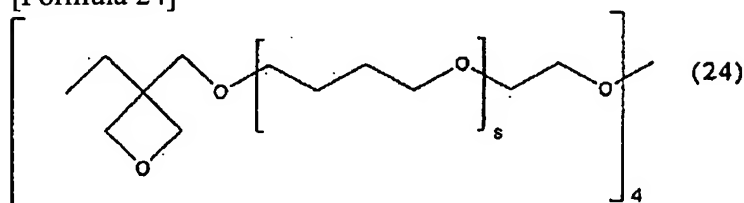
[Formula 23]



[0048] q is 15-100 here.

[0049]

[Formula 24]



[0050] s is 20-200 here.

[0051] In this invention, two or more kinds of the (A) components can be used together.

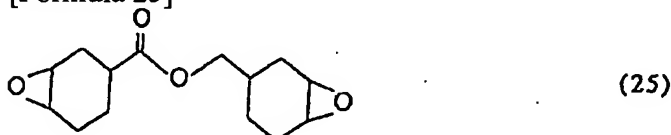
[0052] **** (B)** If a component (B) component is a compound which has one or more epoxy groups in a molecule, both a monomer oligomer and its polymer are usable. (B) As an example of a component, it is usually known as an "epoxy resin" and a well-known aromatic series epoxy resin, cycloaliphatic epoxy resin, an aliphatic series epoxy resin, etc. are mentioned conventionally. In addition, an epoxy resin means a monomer, oligomer, or a polymer below.

[0053] In an aromatic series epoxy resin, the compound with which halogenation of the aromatic series nucleus of these compounds was carried out to a phenol, cresol, the alkylphenol of carbon numbers 2-12, phenylphenol and a PARAKU mill phenol or the monoglycidyl ether of the alkylene oxide adduct of these phenols, and a styrene oxide list is mentioned as what has one epoxy group in intramolecular. **II** or poly glycidyl ether manufactured as what has two or more epoxy groups by the reaction of the polyhydric phenols which has at least one aromatic series nucleus, or the alkylene oxide adduct and epichlorohydrin of those is mentioned. Specifically, the compound with which halogenation of the aromatic series nucleus of these compounds of these was carried out to **II** of resorcinol-diglycidyl-ether; hydroquinone diglycidyl ether; bisphenol A, Bisphenol F, Bisphenol S, a bisphenol fluorene, and the alkylene oxide adduct of these phenols or a poly glycidyl ether; novolak mold epoxy resin; cresol novolak resin; list is mentioned. Besides these, a glycidyl phthalimide, tetra-phthalic-acid diglycidyl ester, o-phthalic-acid diglycidyl ester, etc. are mentioned, and Chapter 2 of the epoxy resin-latest advance - (Shokodo, 1990 issuance), the aromatic series epoxy resin indicated by 4-6 pages of an epoxy resin (the "polymer processing" separate volume 9 and 22nd-volume special number number, a macromolecule publication meeting, Showa 48 issuance) and 9-16 pages are mentioned further.

[0054] Cyclohexene oxide or a cyclopentene oxide content compound therefore obtained is mentioned to carrying out epoxidation of the compound which has cycloalkane rings, such as KISEN or a cyclopentene ring, to at least one cyclo with suitable oxidizers, such as a hydrogen peroxide and a peroxy acid, as cycloaliphatic epoxy resin. As an example, the compound shown by cyclohexene oxide and following type (25) - (27) is mentioned.

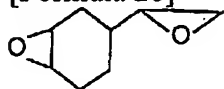
[0055]

[Formula 25]



[0056]

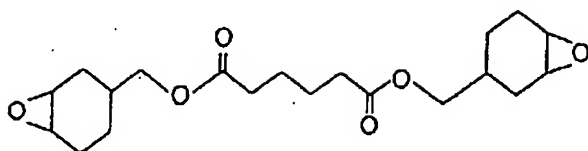
[Formula 26]



(26)

[0057]

[Formula 27]



(27)

[0058] A compound which is indicated by the page 61 of 3.1.5 terms of a UV-EB hardening ingredient [CMC Co., Ltd. and the 1992 issuance], 7 pages of the epoxy resin of said polymer processing separate volume, and 17-28 pages besides these is mentioned. Moreover, these epoxy resins are marketed and have SAIKUROMA M100 (Daicel Chemical Industries), SAIKUROMA A200 (Daicel Chemical Industries), SAIKUROMA M101 (Daicel Chemical Industries), the SEROKI side 3000 (Daicel Chemical Industries), EPOLEAD GT 300 (Daicel Chemical Industries), EPOLEAD GT 400 (Daicel Chemical Industries), etc.

[0059] As an aliphatic series epoxy resin, JI or poly glycidyl ether of fatty alcohol or the monoglycidyl ether of the alkylene oxide adduct, aliphatic series polyhydric alcohol, or its alkylene oxide adduct etc. is mentioned. As an example of monoglycidyl ether, alkyl glycidyl ether, such as butyl glycidyl ether and 2-ethylhexyl glycidyl ether, etc. is mentioned. As an example of JI or poly glycidyl ether Ethylene glycol, propylene glycol, 1,4-butanediol, diglycidyl ether [of alkylene glycol, such as 1,6-hexanediol and its alkylene oxide adduct,]; -- diglycidyl ether [of polyalkylene glycols, such as a polyethylene glycol and a polypropylene glycol,]; -- neopentyl glycol -- diglycidyl ether [of the alkylene oxide adduct of dibromo neopentyl glycol or these glycols]; -- JI of hydrogenation bisphenol A or its alkylene oxide adduct, or poly glycidyl ether; -- trimethylolethane -- JI or triglycidyl ether of trimethylol propane and a glycerol, or the alkylene oxide adduct of these trihydric alcohol; JI of pentaerythritol or its alkylene oxide adduct, The poly glycidyl ether of polyhydric alcohol, such as Tori or the tetra-GURIJIRU ether, etc. is mentioned. Ethyleneoxide, propylene oxide, etc. are mentioned as alkylene oxide here. The aliphatic series epoxy resin indicated by 3-6 pages of said polymer processing separate volume epoxy resin besides these is mentioned.

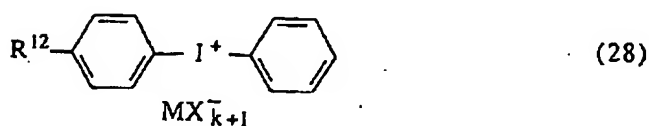
[0060] Furthermore, a compound which there are the epoxy resin which has a triazine nucleus other than these epoxy resins in a frame, for example, TEPIC, (Nissan chemistry), DENAKORU EX-310 (Nagase Brothers formation), etc., and is indicated by 289-296 pages of epoxy resins of said polymer processing separate volume can be used.

[0061] Since it excels in the inner drying property in a thick film, as a (B) component, an aromatic series epoxy resin and cycloaliphatic epoxy resin are desirable. In this invention, two or more kinds of the above-mentioned (B) components can be used together.

[0062] **(C) A component (C) component is a compound which makes cationic polymerization start by the exposure of an activity energy line. As the compound concerned, a variety of compounds conventionally known as an optical cationic initiator can be used. For example, a compound which is indicated by 63-65 pages of 3.1.5th term of said UV-EB hardening ingredient is mentioned. As a desirable thing, a diaryl iodonium salt and a triarylsulfonium salt are mentioned among these initiators. A typical photopolymerization initiator is shown below.

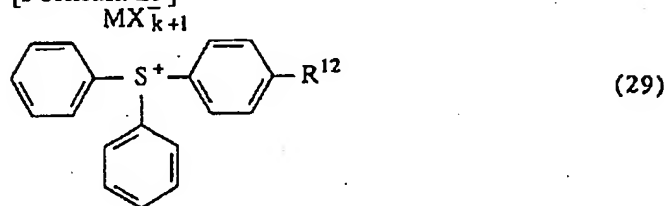
[0063]

[Formula 28]



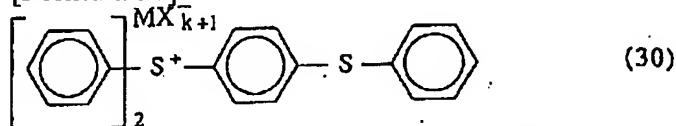
[0064]

[Formula 29]



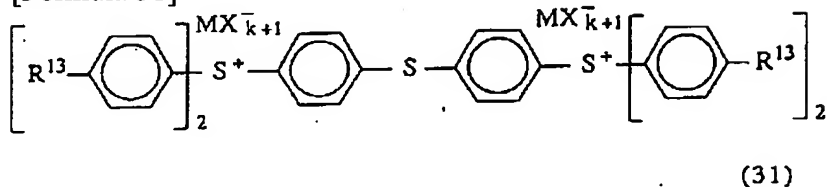
[0065]

[Formula 30]



[0066]

[Formula 31]



[0067] (R¹² is hydrogen, the alkyl group of carbon numbers 1-18, or the alkoxy group of carbon numbers 1-18 among a formula, and R¹³ is a hydrogen atom, a hydroxyalkyl radical, and a hydroxy alkoxy group, and is a hydroxy ethoxy radical preferably.) M -- a metal -- desirable -- antimony -- it is -- X -- a halogen -- it is a fluorine preferably, and k is a metal valence, for example, in the case of antimony, it is 5.

[0068] O Inerts like a cation reactivity compound like a vinyl ether compound, an inorganic bulking agent, a color and a pigment, a viscosity modifier, a processing agent, and an ultraviolet-rays cutoff agent can be blended with the constituent of other component this inventions if needed besides the above-mentioned indispensable component. Moreover, the component in which a radical polymerization is possible can be blended with an activity energy line like the compound and the optical radical polymerization initiator which have an acryloyl (meta) radical if needed.

[0069] When stiffening the constituent of this invention by ultraviolet rays, in addition to the (C) component, a photosensitizer can also be blended in order to improve hardenability further. For the typical sensitizer which can be used in this invention, Crivello is ADOBANSUDO. Inn Polymer science (62 Adv.in Plymer Sci., 1 (1984)) It is possible to use the compound currently indicated. Specifically, a pyrene, perylene, an acridine orange, a thioxan ton, 2-chloro thioxan ton, a PENZO flavin, etc. are mentioned.

[0070] O What is necessary is just to mix the above-mentioned (A) component, the (B) component, and the (C) component according to a conventional method as the manufacture approach of the activity energy-line hardening setup-of-tooling product of manufacture approach this invention of a constituent.

[0071] Here, as for the (A) component, it is desirable to carry out 10-95 weight section combination to the total quantity 100 weight section of the (A) component in a constituent and the (B) component. (A) When the inner drying property in a thick film worsens when the loadings of a component do not fulfill

10 weight sections, and exceeding 95 weight sections, stop hardening. (A) What is necessary is just to determine the blending ratio of coal of a component and the (B) component in consideration of the viscosity of the constituent required of above-mentioned within the limits in practice, the degree of hardness of a hardened material, etc. Moreover, as for the blending ratio of coal of the (C) component, it is desirable to contain at 0.1 - 10% of the weight of a rate to the total quantity of the (A) component and the (B) component, and it is 0.1 - 5 % of the weight more preferably. When not filling this rate to 0.1% of the weight, hardenability is no longer enough objects, on the other hand, when exceeding 10 % of the weight, light transmission nature may become poor, and the inner drying property in a thick film may worsen.

[0072] O The sheet-like optical article of sheet-like optical article this invention consists of a hardened material which said constituent was irradiated [hardened material] and made it harden an activity energy line. As a sheet-like optical article, a Fresnel lens, a lenticular lens, a prism sheet, etc. are mentioned. What is necessary is just to follow the approach currently conventionally performed by manufacture of the article concerned as the manufacture approach of a sheet-like optical article. For example, a constituent is slushed between resin or a metal form, and a transparence base material, and after irradiating an activity energy line and stiffening it, the approach of removing from a mold and manufacturing etc. is mentioned. As a transparence base material, plastic films, such as polyester resin, polycarbonate resin, and acrylic resin, etc. are mentioned to plastic sheets, such as glass, acrylic resin, and polycarbonate resin, and a list. Moreover, what is necessary is just to make **** selection according to the object which also uses the thickness of a lens. As an activity energy line, ultraviolet rays, an X-ray, or an electron ray is mentioned. When irradiating ultraviolet rays, various light sources can be used, for example, low voltage or a high-pressure mercury-vapor lamp, a metal halide lamp, a xenon lamp, an electrodeless discharge lamp, or a carbon arc lamp is mentioned. When making it harden with an electron ray, what various irradiation equipment can be used, for example, a cock loft WARUTOSHIN mold, a BANDE graph mold, or a resonance transformer mold is mentioned, and has the energy of 50-1000ev as an electron ray is desirable, and is 100-300eV more preferably. Since cheap equipment can be used in this invention, it is desirable to use ultraviolet rays.

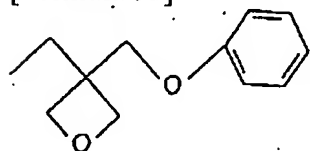
[0073]

[Example] An example and the example of a comparison are given to below, and this invention is more concretely explained to it. In addition, the section in an example and the example of a comparison and % are the weight sections as long as there is no notice especially.

[0074] As an example 1 (A) component, as the following compound (32) 75 section and a (B) component O Following compound (33) [UVR-6110, made in Union Carbide, The alicyclic epoxy compound]25 section is mixed. As a (C) component to this Mixture [UVI-6990 of the hexa fluorophosphoric acid salt of triaryl sulfonium, and propylene carbonate, made in Union Carbide, 50% [of active principles]] was 2-sections-added, it mixed, and the activity energy-line hardening setup-of-tooling product was prepared.

[0075]

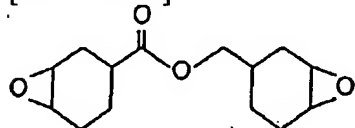
[Formula 32]



(32)

[0076]

[Formula 33]



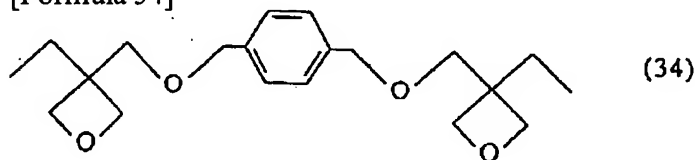
(33)

[0077] After slushing the obtained constituent into the Fresnel lens shuttering made of resin with a thickness of 400 microns and laminating it with a PET film from a top, using the black light (lamp height = 10cm, conveyor speed = 10 m/min, exposure on-the-strength: 780 mW/cm², and 320 mJ/cm²) of the conveyor type which installed the metal halide lamp of 120 w/cm, it let it pass 3 **** (let 10 m/min be an one pass), the constituent was stiffened, and the Fresnel lens was manufactured. The film was removed for the obtained lens from the mold, and the hardenability of a UV irradiation side (upper part) and the interior (lower part) and curvature were evaluated about the mold-release characteristic in that case, and the obtained lens. Measurement of viscosity was measured at 25 degrees C using E mold viscometer. Those results are shown in a table 1. Moreover, the obtained lens was a thing without the engine-performance top problem as a lens.

[0078] O It was used at a rate which shows a compound (32) or the following compound (34) with a table 1 as an examples 2-4 (A) component, and was used at a rate which shows the compound shown in a table 1 as the (B) component and a (C) component with a table 1, and the constituent was prepared like the example 1. It evaluated like [constituent / which was obtained] the example 1. Those results are shown in a table 1. Moreover, the obtained lens was a thing without the engine-performance top problem as a lens.

[0079]

[Formula 34]



[0080]

[A table 1]

| 実施例 | (A) 成分 (部) | (B) 成分 (部) | (C) 成分 (部) | 粘度 * | 硬化性 | | 離型 性 | 反り |
|-----|---------------|----------------|---------------|---------|-----|----|---------|----|
| | | | | | 上部 | 下部 | | |
| 1 | PhOX 75 | UVR-6110 25 | UVI-6990 2 | 30 | ○ | ○ | ○ | ○ |
| 2 | PhOX 75 | YD-128 25 | UVI-6990 2 | 47 | ○ | ○ | ○ | ○ |
| 3 | XDO 50 | UVR-6110 50 | UVI-6990 2 | 200 | ○ | ○ | ○ | ○ |
| 4 | XDO 50 | YD-128 50 | UVI-6990 2 | 225 | ○ | ○ | ○ | ○ |
| 5 | PhOX 90 | YDCN704P 10 | UVI-6990 2 | 35 | ○ | ○ | ○ | ○ |
| 6 | PhOX 75 | YDPN638P 25 | UVI-6990 2 | 137 | ○ | ○ | ○ | ○ |

* : a unit is mPa-s / 25 degrees C [0081]. The code in a table 1 is as follows.

- PhOX : the compound of a formula (32) (compound which has one oxetane ring)
- XDO : the compound of a formula (34) (compound which has two oxetane rings)
- UVR-6110 : the compound of a formula (33) (made in Union Carbide, an alicyclic epoxy compound and YD-128: bisphenol A mold epoxy compound (the Tohto Kasei make, molecular weight about 380 and 2 organic-functions epoxy compound))
- YDCN-704P : cresol novolak mold epoxy compound (the Tohto Kasei make, molecular weight 1900 [about], polyfunctional epoxy compound)
- YDPN-638P : phenol novolak mold epoxy compound (the Tohto Kasei make, molecular weight 570 [about], polyfunctional epoxy compound)
- UVI-6990 : The hexa fluorophosphoric acid salt of triaryl sulfonium, and mixture of propylene carbonate (made in Union Carbide)

[0082] O The constituent was prepared like the example 1 except having used the (A) component and the (B) component, as shown in example 1 of comparison - said 3 tables 2. It was similarly estimated as the example 1 using the obtained constituent. Those results are shown in a table 2.

[0083] O except having used the compound of a radical hardening mold, as shown in example of comparison 4 table 3, it was alike like the example 1, it carried out, and the constituent was prepared. It was similarly estimated as the example 1 using the obtained constituent. Those results are shown in a table 3.

[0084]

[A table 2]

| 比較例 | (A) 成分 (部) | (B) 成分 (部) | (C) 成分 (部) | 粘度 * | 硬化性 | | 離型 性 | 反り |
|-----|-------------------------|--------------------------------|---------------|---------|-----|----|---------|----|
| | | | | | 上部 | 下部 | | |
| 1 | | UVR-6110 100 | UVI-6990 2 | 355 | ○ | × | × | — |
| 2 | | UVR-6110 50 YD-128 50 | UVI-6990 2 | 1672 | ○ | × | × | — |
| 3 | PhOX 75 XDO 25 | | UVI-6990 2 | 29 | × | × | — | — |

* : -- a unit -- mPa-s/25degree-C** : -- the code in a table 2 is the same as a table 1.

[0085]

[A table 3]

| 比較例 | ラジカル硬化型 アクリレート | | 光ラジカ ル開始剤 | 粘度 * | 硬化性 | | 離型 性 | 反り |
|-------|-------------------|--------------|--------------|---------|-----|----|---------|----|
| | | | | | 上部 | 下部 | | |
| 比較例 4 | M-210 75部 | M-305 25部 | Irg184 3部 | 825 | ○ | ○ | × | × |

* : -- a unit -- mPa-s/25degree-C** : -- the code in a table 3 is as follows.

**M-210: ARONIKKUSU M-210, the Toagosei make, bisphenol A ethyleneoxide conversion diacrylate and M-305: ARONIKKUSU M-305, the Toagosei make, a pentaerythritol thoria chestnut rate, Irg184 : the IRUGA cure 184, made in Tiba Speciality Chemicals, 1-hydroxy cyclohexyl phenyl ketone [0086]
[Effect of the Invention] It excels in the inner drying property in the thick film, and hardening contraction is low and practicability is [there is little curvature and / the hardening film is excellent in a mold-release characteristic from a mold, and] the activity energy-line hardening setup-of-tooling product for sheet-like optical articles of this invention has low viscosity, and very high [the film].

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] (A) The activity energy-line hardening setup-of-tooling product for sheet-like optical articles which consists of a compound which makes cationic polymerization start by the exposure of the compound which has 1-4 oxetane rings, the compound which has the (B) epoxy group, and (C) activity energy line.

[Claim 2] (B) The activity energy-line hardening setup-of-tooling product for sheet-like optical articles according to claim 1 whose component is cycloaliphatic epoxy resin.

[Claim 3] (B) The activity energy-line hardening setup-of-tooling product for sheet-like optical articles according to claim 1 whose component is an aromatic series epoxy resin.

[Claim 4] The sheet-like optical article which consists of a hardened material which the constituent indicated by claim 1, claim 2, or claim 3 was irradiated [hardened material], and made it harden an activity energy line.

[Translation done.]